COAL AND CHAR TRANSFORMATION IN HYDROGASIFICATION

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INTRODUCTION

In the present IGT hydrogasification program we have undertaken a study of the petrographic and physical properties of the coals used and the chars produced in the various stages of the gasification process. In the past, we have attempted to study the kinetics and operation of the system without knowing what was really happening to the coal. The usual chemical analyses were conducted, but the results fell far short of indicating what was occurring within the individual coal particles. Also we believed that the identification of what made coal desirable for gasification might hinge on more than the usual coal analysis. We therefore started a study of the petrographic and physical properties of coals and chars with two objectives:

1. To find out as much as possible about what happens to the coal and how it behaves in the process.

2. To develop a correlation between the petrographic properties of coals and their suitability for hydrogasification.

Changes in the process concept as it is developed add to the complexity of the second objective. For example, if pretreatment becomes unnecessary as a result of process improvements, the assessment of a coal's suitability may be substantially modified, as will be shown in this paper. The work reported here applies mainly to the first objective, although it provides a background for the second.

For the process study, seven coals ranging in rank from low-volatile bituminous to lignite have been selected. (Progress of this work is reported in another paper of this symposium.) Of these, two strongly caking coals – Pittsburgh No. 8 and Ohio No. 6 seams – have been selected for the initial and most extensive hydrogasification study because they are the most difficult to process. The work reported here is limited to the Pittsburgh No. 8 coal.

The hydrogasification process consists of three stages that are successive with respect to the coal:

- Pretreatment to destroy the agglomerating power of the coal.

- First-stage hydrogasification, at 1200° to 1300°F, with pretreated coal as feed.

- Second-stage hydrogasification, at 1700° to 2000°F, with first-stage residue as feed.

The resultant chars from each of these stages as well as the initial coal feed have been examined.

PROCEDURES

Petrography

Petrographic work was done with a Zeiss Universal microscope. A 40X Antiflex objective and 12.5X Kpl eyepieces were used for maceral analysis. Reflectance was determined at a wavelength of 548 millimicrons, essentially as described by Schapiro and Gray[5] and by Harrison.[4] A 40X, 0.85 NA achromat "Aufl POL" objective and the same kind of eyepiece as above were used. The aperture in the eyepiece restricted the field to about a 2.5-micron diameter. The Photovolt 520M photometer was modified so that the recorder signal was obtained from a 2000-ohm precision potentiometer. A switch served to connect either the potentiometer or the photometer output meter to the cathodes of the two (reference and signal) tubes of the cathode follower circuits.

Glass standards obtained from Bituminous Coal Research, Inc., were used for reflectance determinations below 2%. For reflectance above 2%, a brilliant-cut diamond was used as a standard.

The fragile, hollow particles of our pretreated coal and hydrogasification residues were crushed and shattered when mounted in epoxy resin by the mounting method usually used for coal, where hydraulic pressure is applied to impregnate the coal. An apparatus and procedure for vacuum mounting was developed which will be described in a later publication.

Particle density was determined by Ergun's gas flow method.[2] The method was shortened by making measurements with only three rates of flow on each of two bed densities. The estimate of the standard deviation from 21 duplicate determinations was 7%.

True density was determined by helium displacement in a Beckman air pycnometer.

Feed Coal and Pretreatment

The Pittsburgh No. 8 coal was obtained from the Ireland mine of the Consolidation Coal Company. Proximate, chemical, sieve, and maceral analyses of the feed in a typical pretreatment run are given in Table 1.

Table 1. TYPICAL ANALYSES OF IRELAND MINE COAL FED TO PRETREATER

Proximate Analysis, wt %	
Moisture	0.9
Volatile Matter	32.7
Ash	14.1
Fixed Carbon	52.3
Total	100.0

Ultimate Analysis (Dry Basis), wt %	
Carbon	67.6
Hydrogen	4.62
Sulfur	4.33
Nitrogen	1.18
Ash	14.22
Oxygen (By Difference)	8.05
Total	100.00

Table 1. TYPICAL ANALYSES OF IRELAND MINE COAL FED TO PRETREATER (Cont.)

Petrographic Analysis, vol % (Mineral-Matter Free)	
Vitrinite	88
Exinite	2
Resinite	(<1)
Fusinite	1
Semifusinite	4
Micrinite	5
Total	100

Sieve Analysis, USS, wt %	
20	3.7
−20 + 30	22.4
−30 + 40	24.8
−40 + 60	25.5
−60 + 80	11.7
−80 + 100	5.2
−100 + 200	4.3
−200 + 325	1.1
− 325	1.3
Total	100.0

The important petrographic characteristics of the coal are the content of: 1) exinite, the group of macerals having the lowest reflectance and highest hydrogen content, 2) vitrinite, the component comprising the bulk of the coal and having an intermediate reflectance and hydrogen content, and 3) inert or semi-inert components having a high reflectance and low hydrogen content. Variation of most of these components in the Pittsburgh seam can be inferred from petrographic analysis by the Bureau of Mines, though these components are reported with a different nomenclature.[3]

Pilot plant pretreatment of the coal to destroy its agglomeration power consists of treating the crushed coal with nitrogen-diluted air in a continuous, single-stage fluid bed at 700° to 800°F. The most striking feature of the pretreated coal particles (Figure 1) is that many have been inflated to thin-walled hollow spheroidal forms. Because of the mixing in the fluid bed and resulting variations in particle residence times, the extent of modification varies greatly from particle to particle. A few have a reflectance as low as that of the original coal and appear to be unchanged, with exinite still present in attrital areas. Appearance of vesicles, disappearance of exinite, and increase in the reflectance occur as the pretreatment progresses. Micrinite becomes difficult to distinguish. An outer zone of reflectance greater than that of the interior appears on most particles. The high reflectance of this skin is attributed to reaction with oxygen; increased reflectance in the mass of the particle may be caused only by carbonization. Reflectance of the skin ranges from 2 to 2.6%; reflectance of the interior ranges from about 0.8%, as observed on the vitrinite of the original coal, up to about 2%. The skin extends into cracks and is present in the interior of some vesicles, though usually with reduced thickness.

A quantitative measure of the swelling during the various stages is given by the average porosity determined for two sieve fractions: 66% on the −30+40 mesh fraction, and 59% on the −60+80 mesh fraction (Table 2).

Hydrogasification Residues

Residues from first- and second-stage runs that are believed to represent typical conditions for the integrated process were chosen for intensive study. In the first-stage run the reactor temperature

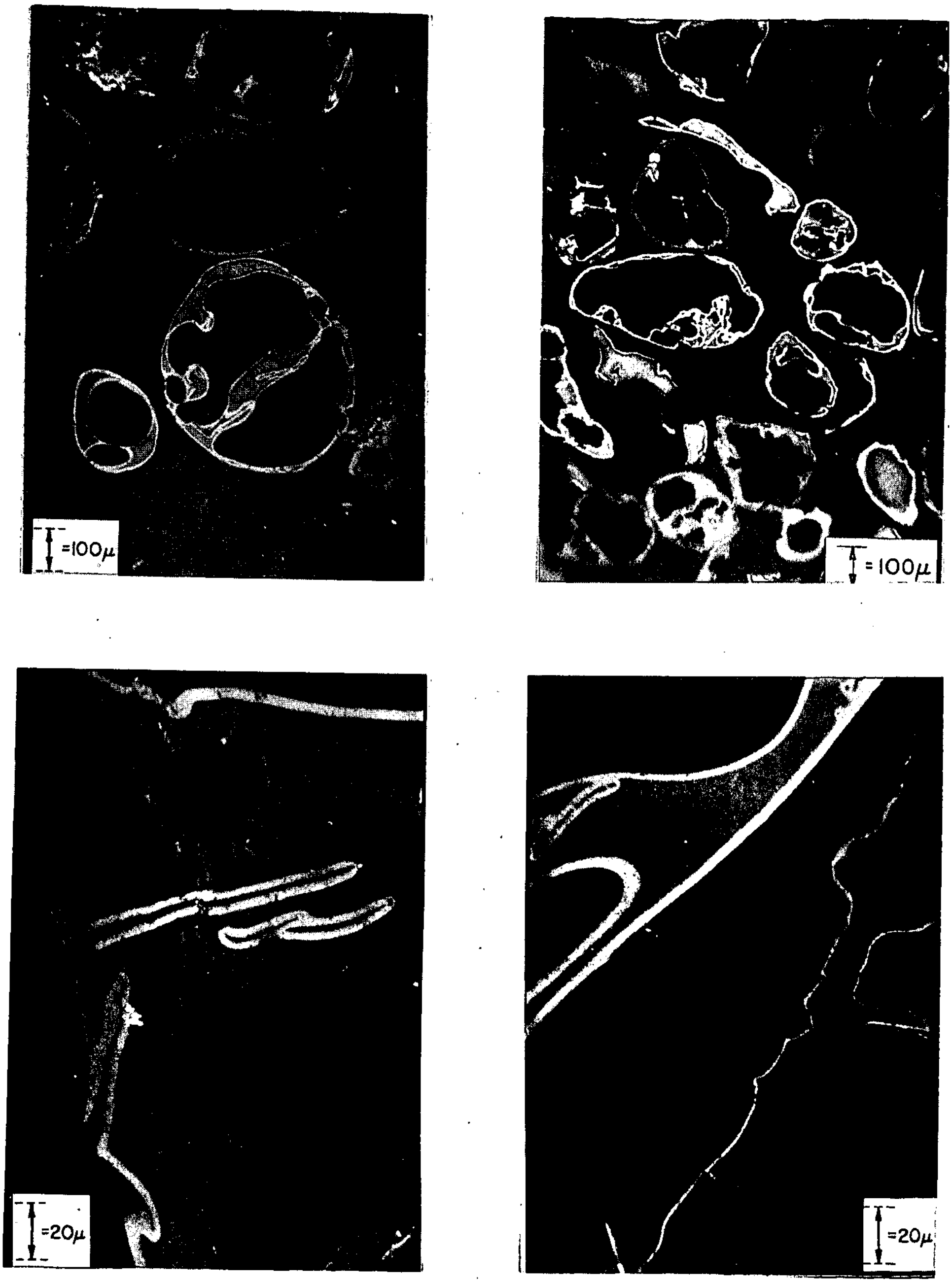

Figure 1. PRETREATED COAL

Table 2. PARTICLE AND TRUE DENSITIES OF HYDROGASIFICATION FEED AND RESIDUE

Sample	Sieve Size, USS	Particle Density, g/cc	True Density, g/cc	Porosity, %	Ash Content (Moisture-Free), wt %
Pretreated Coal	−30+40	0.51	1.52	66	13.7
	−60+80	0.63	1.53	59	15.6
Residue, 1st-Stage Hydrogasification	−30+40	0.48	1.80	73	17.3
	−60+80	0.54	1.77	70	19.1
Residue, 2nd-Stage Hydrogasification	−30+40	0.69	2.10	67	33.0
	−60+80	0.95	2.64	64	54.2
Residue, Free-Fall Hydrogasification	−30+40	0.26	2.13	88	--

averaged 1205°F, and the pressure was 1030 psig. About 21% of the pretreated coal (MAF) was gasified. In the second-stage run the temperature averaged 1825°F, and the pressure was 1023 psig. About 52% of the feed was gasified, equivalent to 41% of the pretreated coal.

In a petrographic examination of the first-stage residue no trace of the high-reflectance skin that is conspicuous in the pretreated coal was present in any particle (Figure 2). Occasional particles of the second-stage residue had a dark skin (Figure 3). Kinship of this dark skin with the pretreatment skin was evident from their similarity in form and in pattern of occurrence, particularly in cracks and around vesicles. While the contrast gives an appearance of darkness to this skin, measurements showed that the reflectance of this "dark" skin was actually greater than that of the skin of the pretreated coal. Evidently the reflectance of the substrate has, during the second stage, increased more rapidly and become greater than that of the skin.

Particles from both first- and second-stage runs showed great variation in both reflectance and structure. Reflectance of the first-stage residue ranged from 2.5% to 7.2%, of the second-stage residue from 3.5% to 8.6% (Figure 4). Some particles appear unchanged in structure from the pretreated coal. In others, additional vesicles, particularly small ones, have formed. In some of the particles the vesicle walls are extremely thin, or have partly disappeared to leave only a skeleton structure. In these highly inflated particles the exterior wall frequently appears more substantial than the interior vesicle walls. This may be an effect of the pretreatment skin.

Particles from a run in which untreated coal was fed were also examined. This coal was from Pittsburgh No. 8 seam but from a different mine — Consolidation Coal Company's Montour 4 mine. The hydrogasification reaction was conducted entirely in 18 feet of free fall. The run could not be completed because of agglomeration of coal in the feed tube and in the reactor. However, the structure of single particles recovered from the base of the reactor is of interest (Figure 5). They are much more uniform in appearance and reflectance than residues from runs with pretreated coal. Almost all of the particles are filled with small vesicles whose walls are perforated. The exterior walls sometimes appear thicker than interior walls, resembling, to some extent, the pretreated coal residue. However, the free-fall particles show numerous exterior wall perforations that are absent in the pretreated coal residue. Also, the particle density and porosity (Table 2) show that the particles have, on the average, swelled much more than pretreated coal.

DISCUSSION

The necessity for pretreatment strongly affects the characterization of high-volatile bituminous coal for hydrogasification. From previous work it is well known that high hydrogen-to-carbon ratio, low rank, and high-volatile matter are conducive to high reactivity and yield in hydrogasification. It is also well known that the reflectance of the vitrinite in a coal is a good indicator of its rank and volatile matter content. Thus, if pretreatment were not necessary, both high exinite content and low reflectance of the vitrinite would be very desirable. However, with the present degree of pretreatment in which

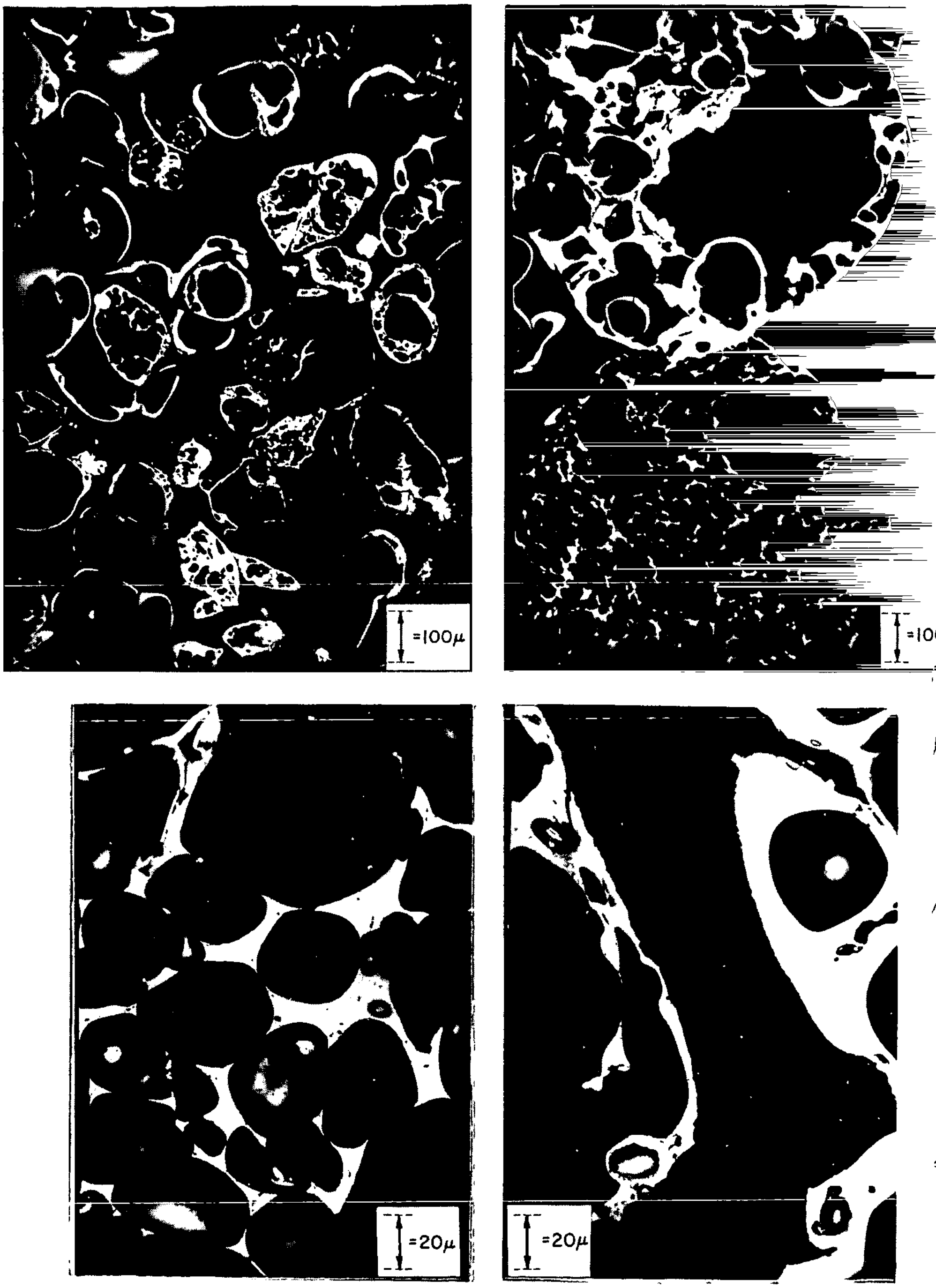

Figure 2. RESIDUE FROM FIRST-STAGE HYDROGASIFICATION

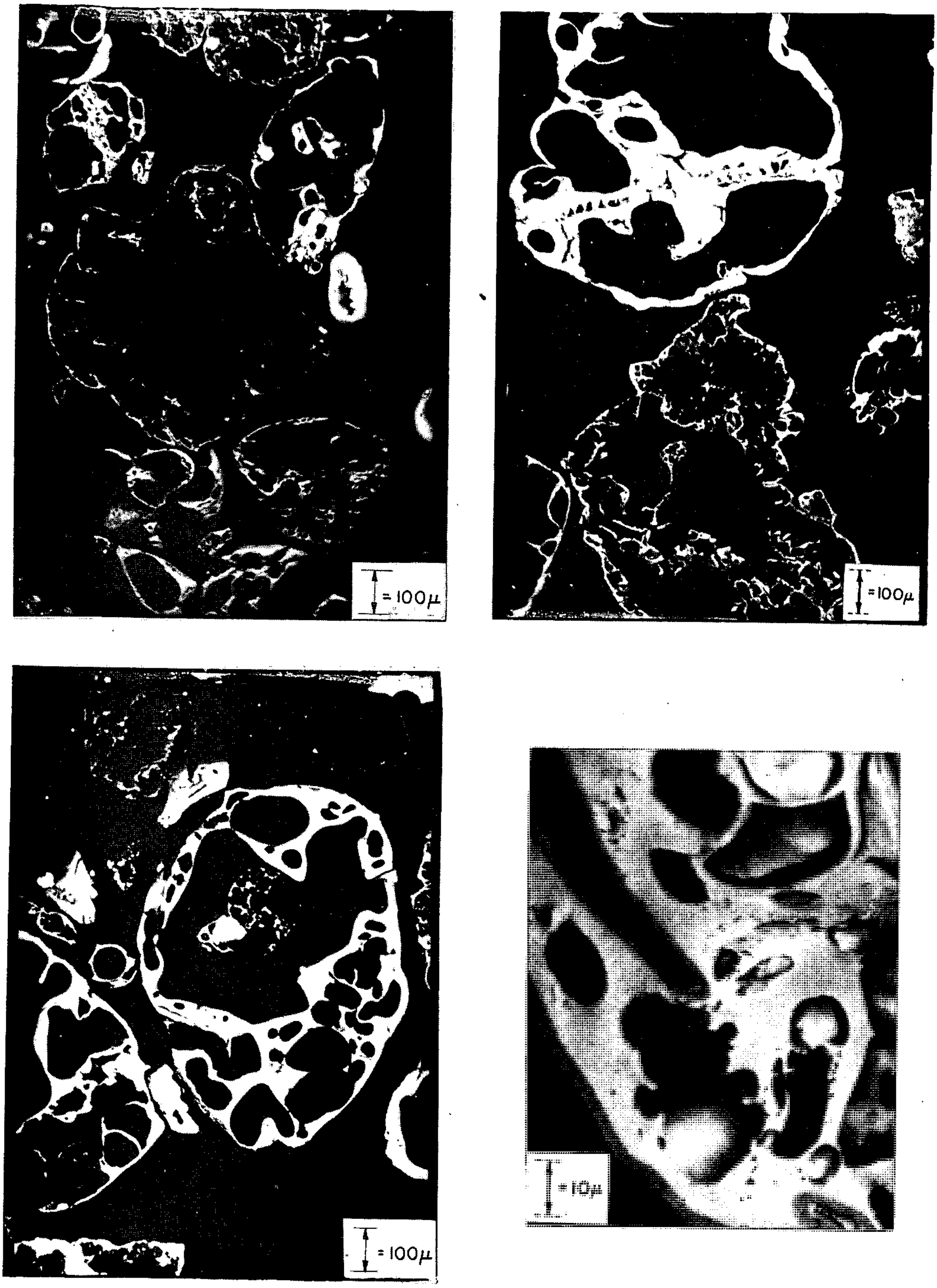

Figure 3. RESIDUE FROM SECOND-STAGE HYDROGASIFICATION

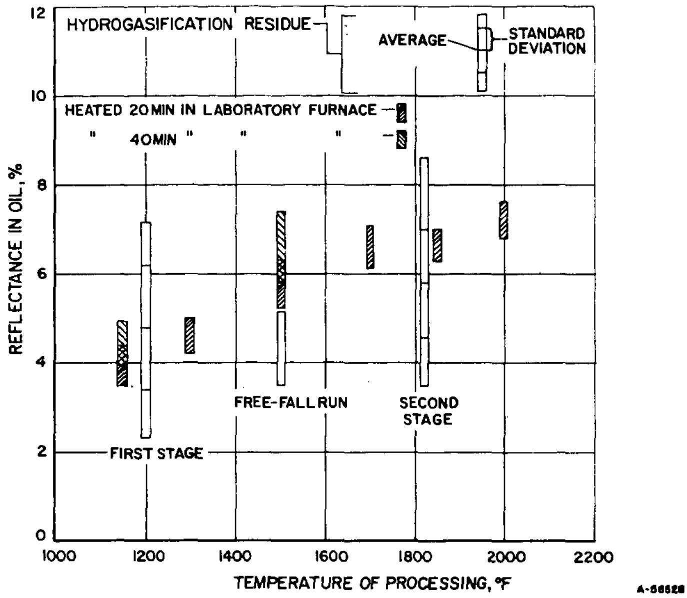

Figure 4. REFLECTANCE OF HYDROGASIFICATION CHARS

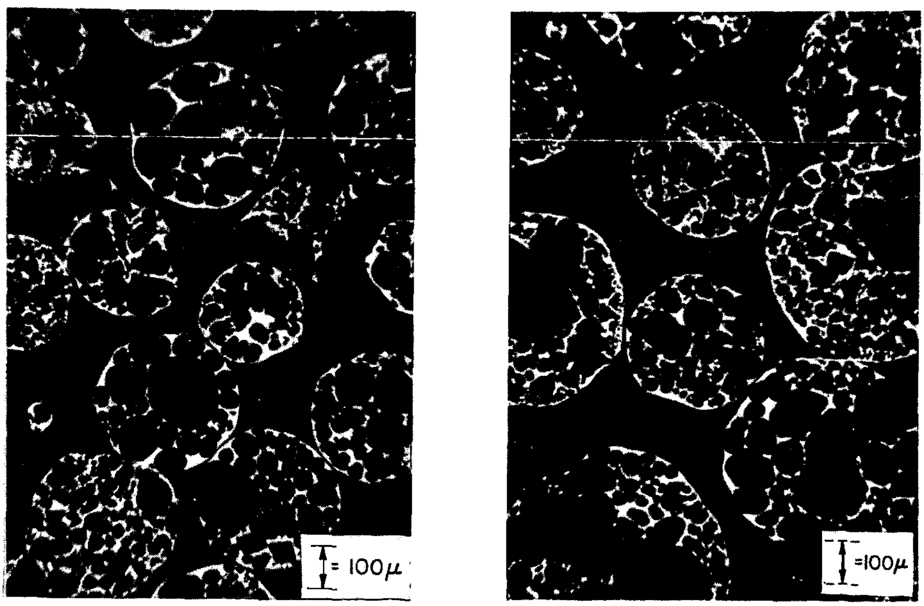

Figure 5. RESIDUE FROM FREE-FALL HYDROGASIFICATION

exinite is almost entirely destroyed, this component is of little value. Similarly, decrease of reflectance of the vitrinite below a yet undetermined level is also of little advantage, because the excess volatile matter is removed in the pretreatment. Thus our second objective — the characterization of coal with respect to its suitability for hydrogasification — is highly dependent on process development in this area. There is some likelihood that in a large commercial plant pretreatment may be avoided.

Pretreatment affects the process in other ways. Sieve analyses of residues from the first stage of hydrogasification show no increase (sometimes a small decrease) in average particle size; thus, essentially no additional swelling of the coal particles occurs in this stage, although the rate of heating is probably as high and the loss of volatiles more than in pretreatment. We attribute the dimensional stability of the particles to rigidity of the pretreatment skin. A few particles that escaped substantial pretreatment probably swell, but this may be balanced by attrition and gas-solid reaction on the exterior surface of the particles. Later runs with less severely pretreated coal show that additional swelling does occur in this stage. This is advantageous because the larger particles present a greater amount of easily accessible surface for reaction. Also, they settle or fall more slowly in free fall, thus providing a longer reaction time for such a stage.

The first-stage residue shows an increase in average porosity (Table 2), which we attribute to gasification of coal in the interior of the particle.

In the second stage of hydrogasification, particle size of the char decreases several percent. We attribute this mainly to attrition, although there may be some decrease in average diameter by way of gasification reactions on the exterior surface. Decreased porosity (Table 2) is attributed to attrition of char particles, which leaves a greater proportion of low-porosity shale particles.

The particle-to-particle variation of the residue in structure and reflectance is of interest because it probably indicates variation in reactivity. The possibility that the subclass of vitrinite in the original coal may have an effect has been considered. There is the well-known differentiation between telenite and collinite. Brown, Cook, and Taylor have suggested a different subclassification: attrital and nonattrital vitrinite.[1] However, many of our coal particles are not composed of a single subclass, while single residue particles are rather uniform in both structure and reflectance. Thus it appears that the history of the particle in the process is a likelier source of the observed variation, although the vitrinite sublcass may have a minor role. Structural variation can easily be explained on the basis of variation in volatile matter content of the pretreated coal, and perhaps also in variation in the thickness of pretreatment skin.

The variation in reflectance is more difficult to explain if it is assumed that a particle's reflectance should be a function of its temperature-time history only. The reflectance variations among residue particles of the three hydrogasification runs that have been discussed are shown in Figure 4. For comparison we also show the reflectance of pretreated coal heated at different temperatures for 20 minutes and 40 minutes. The residues from the two moving-bed hydrogasification runs show much wider variation than either the heated coal or the residue from the free-fall hydrogasification run. The bed temperature, as measured by internal thermocouple, differed by less than 100°F from the average reactor-wall temperature (the normal or reported one) throughout the 36-minute residence of the coal. However, the temperature of individual particles may rise substantially above the bed temperature, because of the heat evolved in the reaction. No explanation of the low reflectance values is available yet.

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